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MASSACHUSETTS
AGRICULTURAL EXPERIMENT STATION

BULLETIN No. 252 JUNE, 1929

Supplements for Copper Fungicides

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Ever since copper fungicides were introduced, numerous supplementary products have been recommended for incorporation in the spray with a view to remedying some real or fancied defect. The contradictory evidence presented by different investigators relative to various supplements may be due in part to differences in amount of substance employed, in method of preparation and of application, but more often to an insufficient number of replications with different crops under varying weather and soil conditions. The use of supplements is not warranted unless they reduce infection and consequent economic losses. This study was undertaken to determine the intrinsic and relative values of the materials recommended for use as supplements.

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AGRICULTURAL EXPERIMENT STATION
AMHERST, MASS.

SUPPLEMENTS FOR COPPER FUNGICIDES

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Introduction

Ever since copper fungicides were introduced, numerous supplementary products have been recommended for incorporation in the spray with a view to remedying some real or fancied defect. This applies particularly to Bordeaux mixture but also to Burgundy and the acetates. In many cases the reputed defects were due probably to faulty methods of preparation or of application, although in some instances the claims were well founded and deserve attention. Most of these shortcomings have been enumerated by different investigators in some form or other and various treatments suggested for their amelioration, of which the following are the most important:

1. To increase the activity of the fungicide by increasing the concentration of the copper ions.
2. To increase suspension by deflocculating the fungicide, by increasing the viscosity of the dispersion medium, or both.
3. To increase wetting power by reducing the interfacial tension at the leaf-spray interface and thereby facilitate spreading and distribution.
4. To increase adhesiveness by forming more resistant deposits.
5. To prevent or reduce crystallization or decomposition by the addition of protectors.
6. To prevent or reduce interactions between fungicides and insecticides in combined sprays.
7. To increase visibility of the deposit.

As a rule supplementary products are added for a specific purpose, but their influence is manifested generally in more than one direction due to the interdependence of the various attributes of a spray. Space does not permit an adequate review of the literature on the subject but attention is called to some of the earlier investigations.

1. To increase the activity of the fungicide by increasing the concentration of the copper ions.

The toxicity of a salt in solution is equal to the combined toxicity of its base and acid or, according to Kahlenberg and True (47)[2] for the various copper salts, to the combined action of its ions; but Coupin (18), Clark (16, p. 37, 40) and Pickering (3, p. 127) have shown that in dilute solutions the action of the acid radical is negligible, although Bain (1, p. 27, 28) noted some exceptions. Pfeffer (73, p. 273, 274) claims that the physiological action of poisons increases with the degree of ionization although undissociated portions may be active, and that non-electrolytes are also poisonous and may undergo chemical decomposition in a way

[1]With the cooperation of Dr. E. F. Guba, Assistant Research Professor of Botany.
[2]Reference is made by number to Literature Cited p. 108.

analogous to the dissociation of electrolytes whereby the poisonous properties are altered. From the above one concludes that the copper in fungicides must not only be soluble but ionized to become active, and that the activity is proportional to the concentration of the copper ions and the potential availability to the total ionizable copper, although the copper in undissociated compounds may undergo decomposition and become appreciably active. Soluble copper in itself is not a true criterion of activity.

A considerable range in activity may be obtained with different fungicides, such as basic, slightly alkaline, neutral, and acid Bordeaux mixtures, Burgundy, the acetates, cuprammoniums and copper sulfate, and with different concentrations; but toxicity to foliage, poor adhesiveness, invisibility and difficulty of preparation practically preclude the use of some of these products. Supplements, however, have been employed by various workers and the process generally consists of adding to Bordeaux or Burgundy mixtures substances known to produce soluble copper in alkaline mixtures. These substances may be divided into three groups (a) sugars, etc. (b) hydroxy-organic acids and (c) biuret compounds. The resulting soluble compound is usually electronegative and the solution purple or violet.

(a) Of the first group may be mentioned sucrose, dextrose, lactose, dextrin and glycerol. They produce soluble copper, but mixtures with dextrose, lactose and dextrin are particularly liable to decompose on standing, with the precipitation of cuprous oxide which is not rated highly as a fungicide.

In numerous tests with Bordeaux 4-2-50 in the station laboratory, soluble copper was observed with 0.016 per cent sucrose, 0.080 per cent lactose, 0.160 per cent dextrin and 0.801 per cent glycerol, but probably occurred in lower concentrations. In most instances the Bordeaux was made with dry, laboratory-prepared hydrated lime after being soaked over night. The amount of added substance varied generally from 0.008 to 0.160 per cent of the spray although larger amounts were employed occasionally.

Many investigators have used sugar and molasses with Bordeaux, Burgundy and special mixtures in field practice. Pons (77), Perret (71, 72) and Barth (cited 5, p. 295, 296) claim that such preparations are more active, non-toxic to foliage and of good suspension and adhesive properties. Doran (22, p. 541) found that sugar and molasses increased the toxicity of Bordeaux to conidia of apple scab fungus. The reaction between Bordeaux and sugar, excluding the calcium hydroxide, is said to be substantially as follows:

$$C_{12}H_{22}O_{11}+H_2O=2C_6H_{12}O_6$$

$$2C_6H_{12}O_6+3O_2=2(CHOH)_4(COOH)_2+2H_2O.$$

$$2(CHOH)_4(COOH)_2+2CuSo_4\ 5H_2O=2(CHOH)_4(COO)_2\ Cu+2H_2SO_4+10H_2O.$$

According to the above equation, 1 part of sugar converts 1.46 parts of copper sulfate into 1.59 parts of copper saccharate and renders soluble 0.37 parts of copper. Investigators recommend generally 5 per cent as much sugar or 10 per cent as much molasses as of copper sulfate which, if applied to Bordeaux 2-2-50 and 4-4-50, would yield approximately 0.01 per cent and 0.02 per cent soluble copper.

(b) Pickering (75, p. 174, 184, 190) and others have shown that hydroxy-

organic acids such as citric, gallic, glyceric, lactic, malic, saccharic, salicylic and tannic acids, in the presence of alkalies, form soluble cupri compounds with a small amount of basic salt in some instances. The structural formulae of the cupri compounds lack confirmation. Organic acids that do not contain alcoholic hydroxyls form insoluble basic salts under the same conditions.

In tests made at this laboratory with Bordeaux 4-2-50, soluble copper was observed with 0.048 per cent gallic, 0.048 per cent pyrogallic and 0.080 per cent tannic acids but probably occurred in lower concentrations. Although hydroxy-organic acids produce soluble copper with Bordeaux and Burgundy mixtures, and are less likely to yield cuprous oxide, there is very little information available relative to their practical use in this connection. The soluble copper produced by the action of sugars and of hydroxy acids in the presence of alkalies is presumably a true solution.

(c) Albuminous substances containing two amino (NH_2) groups linked to different carbon atoms, so-called biuret compounds, also produce soluble copper in the presence of alkalies. Of the more common substances may be mentioned gelatine, glue, casein, albumen, milk and calcium caseinate, although they are seldom employed for this purpose.

In tests with Bordeaux 4-2-50 in the station laboratory, soluble copper was observed with 0.048 per cent glue and 0.160 per cent casein[2]; and in the case of Bordeaux 4-4-50 with 0.05 per cent gelatine, and 0.05 per cent glue; and traces with 0.10 per cent casein and 0.10 per cent albumen on standing 24 hours. In additional tests with Bordeaux 4-4-50 and 0.10 per cent protector, a trace of soluble copper was observed with albumen, increasing with casein and glue to an appreciable amount with gelatine which gave a purple solution. The soluble copper produced by biuret compounds seems to be colloidal as it did not pass a collodian sack and apparently exhibited Brownian movement (Gilligan), but requires further investigation.

All the soluble organic copper compounds mentioned are evidently less active and less toxic to foliage than like amounts of soluble copper in inorganic combination and yet may prove of service in some instances. The supplements may also increase wetting and spreading and possible adhesiveness in the case of some proteids.

2. To increase suspension by deflocculating the fungicide, by increasing the viscosity of the dispersion medium, or both.

The suspension of copper fungicides depends largely on the degree of dispersion and the character of the particles, as added substances seldom have a noticeable deflocculating action but merely retard subsequent agglomeration and increase the viscosity of the dispersion medium. Light amorphous products naturally have a higher power of suspension than those of a dense, crystalline character.

Several references have been noted. Kelhofer (49) claims that sugar increases the suspension of Bordeaux; Neuweiler (65) that 0.01 to 0.20 per cent of tannin is effective; and Winston, Bowman and Yothers (97) that 1 per cent of oil emulsion with Bordeaux 3-3-50 settles less rapidly.

An effort was made to determine the effect of numerous substances on

[2]Dissolved in sodium hydroxide in this instance.

the suspension of Bordeaux mixture made from different batches of dry, laboratory-prepared hydrated lime after being soaked over night. The hydrate was not air-separated and undoubtedly was less uniform in composition and size of particles than many brands of chemical hydrated lime. The relatively lower suspension of the resulting Bordeaux would be expected to respond more readily to the influence of added substances. Considerable variation is inevitable, however, due to inability to control the reaction. Bordeaux 4-2-50 was adopted as preferable to that of a higher lime content, and the amount of added substance (usually called a protector) generally ranged from 0.008 to 0.160 per cent of the spray, although larger amounts were occasionally employed. In the latter case the mixtures were apparently less susceptible to other factors, but excessive dilution of the spray residue is considered objectionable in that it may reduce materially the effectiveness of the fungicide or in some instances even the physiological activity of the plant. The added substance was dissolved or dispersed as thoroughly as possible. With extractives the coarse material was removed by screening. A poorly dispersed protector tends to have an effect on the suspension of Bordeaux similar to that of coarse particles of lime. In some instances the inherent properties may be more than offset by poor dispersion. The solution of copper sulfate was added to the soaked hydrated lime and then the protector added, thoroughly mixed and suspension readings taken at the end of 1, 2 and 3 hours. These tests were conducted in rubber-stoppered, glass museum jars of the following dimensions: total height, 305.5mm (14 inches); length and outside diameter of the body, 303.0 by 63.5 mm (13.0 by 3.5 inches) and capacity to the neck, 850 to 900 cc. The length of the column for a volume of 780 cc was determined for each jar and the results calculated in percentage.

Among the substances tested were sugars, dextrin, starches, gums, gum resins, soapbark extract, pectin extracts, mucilaginous extracts, miscellaneous extracts, glycerol, proteids, organic acids, salts of organic acids, soaps, inorganic salts, earths, etc. The data are too voluminous to permit their publication in entirety, but by excluding most mixtures that settled more than 10 per cent an hour, a reasonable tolerance, many of the substances are eliminated entirely and only average results are reported on those retained. The averages do not represent an equal number of tests. As a rule, the more promising the results, the more determinations were made in confirmation. An increase in suspension with an increasing amount of substance within limits that are permissible, and the uniformity of results with a given amount, were considered a criterion of the effectiveness of the substance employed.

The sugars—dextrose, lactose, levulose, manitose and sucrose—did not appear to have an appreciable influence on the suspension of Bordeaux 4-2-50 although occasionally a test with 0.016 per cent came within the tolerance. Powdered dextrin, British gum, arrowroot-starch (Maranta), inulin (Alant) and soluble starch (amylo-dextrin) did not increase suspension within the limits tested. Gum arabic (Acacia), at the rate of 0.080 to 0.160 per cent may have had a slight influence, but tragacanth proved less satisfactory although tests of 0.024 per cent were passable. Several gum resins were employed but required a solvent and did not increase suspension.

Soapbark (Quillaja) extract containing saponin had no effect. Several

pectin extracts were tested, of which fruit pectin proved of no value; agar-agar, at the rate of 0.024 to 0.048 per cent, probably some; Iceland moss (Cetraria), less and not dependable; and Irish moss (Chondrus), of no value. The mucilaginous extracts were slightly more promising:—no increase in suspension was obtained with licorice (Glycyrrhiza); slight increase, with 0.080 to 0.160 per cent of linseed (Linum), both flaxseed meal and the fat extracted residue; considerable increase, with 0.016 to 0.160 per cent of quinceseed (Cydonia); and slight increase, if any, with slippery elm (Ulmus). Miscellaneous extracts from corn stover, hay and rye straw, used at the rate of 0.801 to 1.603 per cent, increased suspension appreciably; but to ascribe their action to definite compounds would be difficult. Glycerol was of no value. Of the proteids, neither gelatine nor glue increased suspension. In subsequent tests, 0.10 per cent of albumen, casein, gelatine and glue with Bordeaux 4-4-50, using chemical hydrated lime, did not increase suspension. Albumen and casein would not disperse satisfactorily in water.

Various organic acids—butyric, citric, gallic, lactic, pyro-gallic, tannic and tartaric acids—were employed, of which tannic acid at the rate of 0.016 to 0.080 per cent improved suspension. Salts of organic acids, such as calcium caseinate, sodium albuminate, benzoate, caseinate, oleate and resinate, gave no increase. Several of these substances were laboratory prepared and probably carried an excess of sodium hydroxide. Castile and resin soaps were of no apparent value, but soap powder at the rate of 0.016 to 0.801 per cent increased suspension. Soaps are objectionable, however, in that they react with lime on standing to form a curdy precipitate.

Of the inorganic substances, calcium and magnesium silicates and aluminum hydroxide proved of no value, but liquid sodium silicate at the rate of 0.032 to 1.603 per cent, increased suspension. The dry silicate was less effective. Bordeaux so treated, however, tends to peel from the leaves on drying (Dunbar). Bentonite, clay, fuller's earth, infusorial earth, Perkin's earth, talc and Wilkinite were also employed. Of these, 0.016 to 0.160 per cent of Bentonite and 0.048 to 0.160 per cent of Wilkinite proved of value. These are yellow "ball" clays of similar characteristics, and with fungicides, other than Bordeaux with excess lime, may serve to increase the visibility of the spray residue.

The results obtained with the more promising supplements affecting suspension are reported in Table 1.

Tannic acid, Bentonite and Wilkinite were the most dependable substances employed for increasing the suspension of Bordeaux mixture, although quinceseed extract, soap powder and sodium silicate deserve mention. Other substances may prove serviceable under different conditions or in larger amounts; but whether their use with a more highly dispersed lime is warranted, is an open question and depends somewhat on other considerations such as ability to increase wetting, spreading and adhesiveness and to retard decomposition. Lovett (58) claims that suspension in itself is a fair indication of power to spread, and most workers will concur in principle. The substances reported may prove of value with other copper fungicides but probably not to the same degree.

Table 1.—Suspension of 4-2-50 Bordeaux with Various Supplements.

Supplement	Hours	Percentage of Supplement Added: 0.000	0.008	0.016	0.024	0.032	0.048	0.080	0.160	0.801	1.603
		Percentage Suspension									
Check (average 28 tests)	1	82.1	...	...	...	...	...	...	...	...	...
	2	62.8	...	...	...	...	...	...	...	...	...
	3	53.0	...	...	...	...	...	...	...	...	...
Gums											
Arabic	1	...	91.0	82.9	92.4	85.9	91.1	91.9	91.6	...	...
	2	...	61.9	65.2	73.3	75.4	82.0	83.2	83.5	...	...
	3	...	49.9	56.8	57.4	68.0	74.0	73.9	76.3	...	...
Tragacanth	1	...	91.0	85.9	90.8	72.7	70.9	...	...	...	...
	2	...	79.9	69.9	81.5	64.3	64.2	...	...	...	...
	3	...	65.9	60.7	72.0	60.1	60.7	...	...	...	...
Pectin Extracts											
Agar-Agar	1	...	90.9	89.3	91.6	88.4	89.7	81.1	...	...	...
	2	...	66.9	79.3	81.6	68.5	80.9	73.0	...	...	...
	3	...	55.7	70.8	71.0	70.8	74.5	68.7	...	...	...
Iceland Moss	1	...	87.9	90.8	86.7	84.7	85.6	94.1	...	...	...
	2	...	67.1	77.0	65.7	61.0	62.0	87.2	...	...	...
	3	...	55.2	67.5	56.6	53.9	55.6	79.8	...	...	...
Mucilaginous Extracts											
Flaxseed Meal	1	...	...	80.9	...	89.4	90.5	90.9	93.4	...	...
	2	...	...	59.2	...	72.9	74.2	80.0	85.7	...	...
	3	...	...	53.5	...	59.1	62.9	69.8	78.3	...	...
Linseed Meal (ether extracted)	1	...	...	77.7	...	70.9	76.8	89.4	...	...	...
	2	...	...	64.6	...	58.3	73.7	78.9	...	...	...
	3	...	...	56.5	...	53.1	62.8	69.7	...	...	...
Quince Seed	1	...	92.0	92.3	90.6	92.2	92.3	94.1	96.2	...	...
	2	...	81.1	83.3	80.5	83.3	84.4	88.1	92.4	...	...
	3	...	69.4	74.3	71.5	74.1	76.8	82.1	88.2	...	...
Slippery Elm	1	...	85.9	89.7	...	90.8	88.7	94.4	...	...	...
	2	...	59.9	78.4	...	79.9	67.6	86.3	...	...	...
	3	...	47.2	65.5	...	68.0	58.4	74.4	...	...	...
Miscellaneous Extracts											
Corn Stover	1	...	...	...	...	...	87.6	84.4	87.9	96.5	97.5
	2	...	...	...	...	...	63.5	66.0	65.6	92.6	94.7
	3	...	...	...	...	...	56.0	58.9	58.9	89.1	91.9
Hay	1	...	...	...	...	...	90.1	80.5	91.1	95.1	95.8
	2	...	...	...	...	...	76.9	61.3	81.6	89.8	91.2
	3	...	...	...	...	...	64.2	55.3	71.3	84.2	86.7
Rye Straw	1	...	...	...	...	...	...	...	...	92.6	94.4
	2	...	...	...	...	...	...	...	...	84.2	88.5
	3	...	...	...	...	...	...	...	...	75.1	82.5
Organic Acids											
Tannic	1	...	...	91.7	...	93.7	95.0	95.4	...	...	...
	2	...	...	82.2	...	85.8	88.7	89.7	...	...	...
	3	...	...	73.1	...	77.4	82.3	84.5	...	...	...
Soaps											
Powder	1	...	...	90.8	...	90.9	92.5	92.9	92.7	97.2	81.6
	2	...	...	80.6	...	80.7	83.9	85.3	84.7	89.6	67.0
	3	...	...	70.4	...	70.5	75.3	77.4	77.2	83.7	57.6
Inorganic Salts											
Sodium Silicate (liquid)	1	...	...	92.5	...	92.0	91.2	92.6	94.2	97.2	96.8
	2	...	...	80.4	...	83.9	81.9	84.8	87.6	93.3	93.5
	3	...	...	70.0	...	75.9	72.3	75.5	79.6	89.0	90.0
Sodium Silicate (dry)	1	...	...	88.3	...	...	90.4	90.8	93.6	...	...
	2	...	...	74.8	...	...	80.1	80.5	86.2	...	...
	3	...	...	60.6	...	...	69.9	70.6	78.7	...	...
Earths											
Bentonite	1	...	89.0	92.5	...	92.2	...	96.4	96.4	...	...
	2	...	73.4	81.6	...	84.0	...	92.5	91.5	...	...
	3	...	59.6	71.6	...	75.9	...	87.2	86.9	...	...
Wilkinite	1	...	...	...	...	...	94.3	95.7	96.6	...	...
	2	...	...	...	...	...	88.3	90.8	92.9	...	...
	3	...	...	...	...	...	82.3	85.8	89.0	...	...

3. To increase wetting power by reducing the interfacial tension at the leaf-spray interface and thereby facilitate spreading and distribution.

A highly dispersed copper fungicide assures better suspension and more uniform distribution than one of larger aggregates, especially when applied as a mist or film of invisible drops. Greater adhesiveness of the resulting residue is also obtained. Drench applications on the other hand are more likely to collect in drops, particularly on the edge of the leaves, or run off carrying most of the fungicide. The force with which the spray is applied is also a factor in wetting and spreading. The resistance of leaves to wetting varies with the character of the leaf surface (epidermis) and the nature of the spray solution. The epidermis of leaves may be a relatively thin membrane of cellulose or heavily cutinized (cuticularized), waxy, hairy, etc., and differs greatly in respect to wetting. The same applies in a measure to fruits, buds, spurs and older growth. The leaves of apples, peaches, pears and grapes are cutinized, and fruits like apples and plums and the leaves of the cabbage are waxy and not easily wet as they interpose a film of air between the leaf and spray. In most instances, the addition to the spray of organic substances of similar constitution to those in the plant, i. e., albuminous substances and plant infusions, and their adsorption or surface concentration at the leaf-spray interface, reduces the interfacial tension and permits the spray to touch, wet and form a continuous film over the surface. In the case of waxy surfaces, the substances added generally have a fairly large molecule with a small, active group soluble in water and with the inactive portion adsorbed in the surface layer of the spray solution. When the inactive portion is similar to or soluble in the wax, its adsorption at the leaf-spray interface reduces the interfacial tension and permits the spray to spread. Soap and soap emulsions, when compatible with the fungicide, are usually effective on such surfaces and other substances will be noted.

It is evident, therefore, that wetting is essentially the same on all plant surfaces and that an effective solute must have a low surface tension (soaps), or the property of surface concentration (saponin, proteids), and, in some instances, a solvent action on the epidermal coating in addition. Since there is no method for measuring interfacial tension between plant surfaces and spray and as the nature of the surface interposed by the plant is problematical, it is impossible to foretell the action of added substances known to reduce surface tension of the spray solution on the plant surface-spray interface. The fact remains, however, that an increase in wetting and spreading is necessary in many instances, is desirable in all cases, and is secured mainly by reducing the interfacial tension. Therefore, the substances to be added for the various leaves, fruits and other surfaces must be determined largely by trial and error.

Theory of Wetting and Spreading.

Numerous investigators have contributed extensively on the subject and a few will be noted. Mausier (62), Gastine (32) and Ruth and Kelly (82) found a low surface tension of the spray favored spreading. Brunnich and Smith (6) assert that wetting power depends primarily on surface tension. Lovett (58) claims that neither suspension nor viscosity of the spray solution is a true index of spreading but considers suspen-

sion indicative and later (59) a desirable attribute, although not a definite criterion. Vermorel and Dantony (90) state that spreading occurs when the cohesion of the molecules of the liquid is less than double their adhesion for the solid and correlate a low "static" surface tension with spreading, but subsequently decided (91) that it is not an index and that a high surface viscosity has greater influence. Lefroy (56) states there are three surface tensions—spray, leaf and interface—involved in spreading and that the first should be low but the others cannot be determined. Willows and Hatschek (96) claim that the adsorption or concentration of a solute at the liquid-solid interface reduces interfacial tension. Cooper and Nuttall (17) accept the Quincke (79) theory,—that if the surface tension of the solid is greater than the sum of the surface tension of the spray and of the interface, spreading will occur; but believe the solvent action of the spray on the solid and the surface concentration of the solute, with a high surface viscosity, may vitiate the equation. They consider that interfacial tension alone will suffice for comparative purposes, and with soap solutions is directly proportional to the drop number (stalagmometer reading), since spreading varies inversely with interfacial tension. The general formula for the wetting of a solid by a liquid, as given by Nuttall (66, p. 38), is as follows:

$$T_2 \text{ must be } > T_1 \div_{12}$$

T_1 surface tension of liquid/air.
T_2 surface tension of solid/air.
T_{12} interfacial tension of liquid/solid.
Thus, spreading can be increased by reducing the surface tension of the spray or of the leaf-spray interface and T_2 and T_{12} are indeterminate.

Freundlich (26, cited 66, p. 39) points out that a liquid may not wet the surface of some solids owing to its inability to dissolve the surface layer of moist air adsorbed on them, and sometimes the wetting power of a liquid (saponin, proteids) is higher than would be expected, due to an exceptional power of surface concentration (capillary adsorption) manifested by a superficial viscosity first observed by Plateau (76) and later by Vermorel and Dantony (91). Donnan (21) and Hillyer (43, p. 524) have shown that a soap solution acts as an emulsifier by virtue of its low interfacial tension. Ruth and Kelly (82) claim that direct impact and drenching favor the formation of a film. Harkins, Brown and Davies (37), Harkins, Davies and Clark (38) and Langmuir (51) treat various phases of interfacial tension, influence of the size and shape of the molecule, active and inactive portions, orientation, etc. Moore (64), Nuttall (66) and Taylor (88) present a review of the subject and its present status.

Substances Employed.

The substances that have been used by different investigators to increase wetting and spreading include substantially all those that were employed in this Station for increasing suspension (Sec. 2) and in addition emulsions, creosote, some phenol derivatives and several of the higher alcohols. There is apparently a clear line of demarcation between wetting, spreading and distribution and adhesiveness and yet the two issues are sometimes confused. Furthermore, the results are generally based on the character of the wetting and the visible deposit on the foliage—a matter

of personal judgment, however careful the observations. Most of the experiments cited apply to foliage having a thin cellulose or cutinized epidermis, and those pertaining to waxy leaves and fruits are so designated. The theory that "like attracts like" may have unduly influenced practice in some instances.

Attention is called to the results of other investigators. Recent data on sugar and dextrin have been seldom noted. The use of saponin to increase spreading was probably first recommended by Gastine (32) and later by Chappaz (13) and Lafforgue (50). Cactus (Cereus) extract, containing cactine, apparently has a similar action and was found by High (42) to increase the spreading of arsenites. Irish or Pearl moss (Chondrus), so-called carrageen, was employed by Issleib (46) and, according to Stearns (86, p. 9-13), facilitates the distribution of arsenicals. Lovett (58) found that sage tea increased the spreading of arsenicals on plain but not on waxy surfaces (59). Vermorel and Dantony (94) claim that 0.05 per cent of casein increases the spreading of Bordeaux on grape vines, and Stearns (86, p. 9-13) and Smith (85) that calcium caseinate increases the spreading of lead arsenate. Some workers report casein of 0.003 to 0.03 per cent (probably with alkali) an effective spreader. David (78) employed 0.75 per cent of glue with Bordeaux but later (63) decided it was of no particular value. Lowe (60) states that glue increased the spreading of lead arsenate. Hawkins (40, p. 22-25) found that 0.50 per cent of glue, fish-oil soap and rosin fish-oil soap reduced the surface tension of Bordeaux 4-2-50 and their efficiency increased in the order named. Galloway (28, p. 220, 221; 29, p. 202, 203, 213; 30, p. 131), Fairchild (24) and Swingle (87) found soaps increased the wetting and spreading of copper fungicides, and Washburn (95) that 1.50 per cent of whale-oil soap increased the spreading of Paris green and apparently the adhesiveness. Trappmann (89) found soap the cheapest wetting material but unsafe to use with arsenicals. Sodium oleate and sodium resinate are occasionally suggested as substitutes. Various earths and other inorganic substances have been used but proved of little value as spreaders.

Oil emulsions, soap emulsions of creosote and saponin emulsions of creosote (32) are said to increase spreading on all surfaces but are seldom employed with copper fungicides. Pickering (74, p. 2010, 2011; 2, p. 29) recommended a stable emulsion prepared from copper sulfate, calcium hydroxide and a high-boiling distillate, but data relative to its efficiency are not available. Winston, Bowman and Yothers (97) claim that 1 per cent of oil emulsion with Bordeaux 3-3-50 increased spreading on citrus. Moore (64, p. 18, 19) found beechwood and coal tar creosotes, phenol derivatives, such as carvacrol, eugenol and xylenols, and amyl and benzyl alcohols excellent for waxy surfaces.

Among the points that should be considered are compatibility with the fungicide, effectiveness in wetting and spreading, ease of preparation and cost. The evidence presented is drawn from special experiments with basic copper sulfate by Dr. E. F. Guba of the Market Garden Field Station at Waltham. He employed cucumbers and tomatoes in the greenhouse and cucumbers and celery in the field. The amount of substance added is reported on the basis of the spray—0.10 per cent is equivalent to 3.8 grams (0.13 oz.) to an American gallon, or 188.5 grams (6.65 oz.) to the barrel. He found that basic copper sulfate had rather poor wetting and spreading properties as compared with Bordeaux 4-4-50. With

0.10 per cent of sugar or 0.05 to 0.15 per cent of dextrin no improvement was observed. With 0.10 to 0.21 per cent of Tekoe flour a slight increase was reported and with 0.10 per cent of wheat flour "fair" spreading obtained. Starchy products have to be dispersed (gelatinized) before use, and in the case of flour and its by-products the addition of dilute caustic soda or potash probably increases their effectiveness by dissolving the proteids. Alkali was not employed in this experiment. With 0.05 to 0.15 per cent of gum arabic (Acacia) poor wetting and spreading were secured, which probably holds true for tragacanth.

Soapbark (Quillaja) extract and 0.03 to 0.10 per cent of technical saponin gave excellent spreading. Guba did not commend either gelatin or soluble albumen at the rate of 0.05 to 0.10 per cent but obtained excellent wetting and spreading with the same amount of glue. Gelatine and glue have to be dispersed in warm water, and a high-grade animal glue requires aging to develop its maximum efficiency as an adhesive. Possibly a low-grade animal glue which is more readily soluble or a fish glue might serve in this connection, although there is no evidence to that effect. Albumen, casein, dried blood, egg-powder and other nitrogenous substances require a small amount of alkali for proper dispersion. With 0.10 per cent of skim milk powder, good spreading was secured; but an equivalent amount, in dry matter, of semi-solid buttermilk proved less satisfactory and about equal to Tekoe flour. No alkali was added. With 0.10 to 0.13 per cent of calcium caseinate, a commercial preparation, excellent wetting and spreading were obtained. Laucksite, a soy-bean—fish-oil adhesive, proved less satisfactory. With 0.10 per cent of Castile soap, 0.10 per cent of Ivory soap and 0.05 to 0.75 per cent of rosin fish-oil soap, excellent spreading was secured—even better in the case of rosin fish-oil soap than with calcium caseinate. The resulting curdy precipitate on standing was objectionable with all soaps. Soaps are effective on both plain and waxy surfaces, although the amount may have to be increased to 0.20 to 0.25 per cent in the latter case. With 0.10 per cent of Wilkinite poor wetting and spreading were obtained.

In Guba's experiments saponin, glue, calcium caseinate and soap proved the most efficient of the substances tested, although wheat flour deserves mention. Some albuminous substances may react with the copper to form soluble compounds as previously shown (Sec. 1). Soap mixtures should be applied immediately after preparation to avoid the formation of a curdy precipitate. The cost of most of the supplementary products is negligible as compared with labor, but the reduction in amount of infection due to better distribution of the fungicide is not always appreciable according to our Station observers. This may not hold equally true on waxy surfaces.

4. To increase adhesiveness by forming more resistant deposits.

The degree of dispersion and uniformity of distribution are important factors in the adhesiveness of copper fungicides. An increase in spreading assures better distribution and generally a more persistent and protective deposit. Many investigators endeavor to increase adherence still further by the formation of more resistant deposits. If carried too far, however, the fungicidal action may be impaired and the physiological activity of the plant reduced materially by the impenetrable coating on the surface which is particularly noticeable in the case of certain emulsions.

Numerous investigators have contributed to this phase of the subject. Perret (71) employed 0.20 per cent molasses with Burgundy mixture; Galloway (27, p. 10, 21), molasses with Burgundy on grapes; Gastine (31), molasses with Bordeaux; and Perraud (69), molasses with Bordeaux on grapes and evidently considered it beneficial. On the other hand, Girard (34) used 2 per cent molasses with Bordeaux on potatoes, Guillon and Gouirand (35, 36), 1 per cent molasses with Bordeaux on grapes; Lavergne (52), sugar with Bordeaux; Kelhofer (48), 0.10 per cent sugar with Bordeaux and Burgundy mixtures; and Butler and Smith (10, p. 441), 0.10 per cent sugar with Bordeaux and concluded that molasses and sugar were comparatively inefficient or reduced adherence. Kelhofer (48) found that 0.10 per cent sugar increased the adhesiveness of both neutral and basic copper acetates, especially the latter. Fernald (25, p. 6) recommended glucose or molasses as a sticker for lead arsenate. Lowe (60) found glucose inefficient with lead arsenate. Perraud (69) claimed that dextrin and starch with Bordeaux were of no value, but Patrigeon (68) stated that 0.50 per cent of dextrin increased adhesiveness. Parker (67) found that flour increased both spreading and adhesiveness of lead arsenate, and Headlee (41, p. 294) that flour doubled the adherence. Perraud (69) found gum tragacanth fairly efficient.

Stearns (86, p. 9-13) reported that Irish moss (extract) increased the adherence of arsenicals. Guillon and Gouirand (35, 36) found 0.30 per cent of gelatine with "acid" Bordeaux of little or no value, and Butler and, Smith (10, p. 437, 442) obtained similar results from casein with Bordeaux 4-4-50. Butler and Smith (11, p. 284-286) found, however, that 0.05 per cent of gelatine increased materially the adhesiveness of neutral and basic copper acetates. Vermorel and Dantony (93) had previously noted this effect and also claimed (92) that 2 per cent of casein renders all alkaline copper sprays adherent to grape vines, recommended (93) casein for Bordeaux and showed (94) that 0.05 per cent increased the adherence of Bordeaux to grape vines. Chauzit (15), Degrully (19) and the Iowa Experiment Station (45) considered casein effective with Bordeaux; and Lecomte (53), that 2 per cent of milk increased the adhesiveness of Bordeaux 8-4-50. Headlee (41, p. 294) found that calcium caseinate or powdered skim milk more than doubled the adherence of lead arsenate. Perraud (69) claimed egg powder and dried blood inefficient with Bordeaux, while Cazeneuve (12) reported egg white and dried blood very effective. Galloway (27, p. 10, 21) secured good results from glue with Burgundy (although 3.5 per cent proved injurious); and Perraud (69, 70), from glue with Bordeaux. Lowe (60) increased the adherence of lead arsenate with glue; and Stearns (86, p. 9-13), that of arsenicals with calcium caseinate. Lees (54) employed glue, flour and a mixture (55) of whiting, glue and potassium bichromate as stickers for cover washes. Neuweiler (65) claimed that 0.01 to 0.20 per cent of tannin increased the adherence of Bordeaux. Perraud (69) observed that rosin increased the adhesiveness of Burgundy; Ravaz and Bonnet (80), that resin slightly increased the adherence of Bordeaux; Sirrine (84), that a resin-lime mixture increased the adhesiveness of Bordeaux and Paris green to cabbage and cauliflower; and Gillett (33), that sodium resinate increased the adhesiveness of arsenites. Guillon and Gouirand (35, 36) found that 3 per cent of soap with Burgundy and 2 per cent with Bordeaux increased adhesiveness; Perraud (69), that 3 per

cent of soap increased the adhesiveness of Bordeaux; Chuard and Porchet (14), that soap increased adherence on grapes; Shear (83), that rosin fish-oil soap increased the adhesiveness of Bordeaux on cranberries; Hawkins (39, 40 p. 19), that rosin fish-oil soap increased the adherence of Bordeaux on grape leaves, and that 0.50 per cent of fish-oil soap and rosin fish-oil soap increased the adherence of Bordeaux 4-2-50 on grape berries (40, p. 25); and Washburn (95), that 1.50 per cent of whale-oil soap or soft soap increased both spreading and adhesiveness of Paris green. Dye and Newhall (23) found that 2 pounds of resin-fish-oil soap in 50 gallons increased the adhesiveness of Bordeaux 5-5-50 to celery and possibly served as a spreader. Berger (4) claimed that 3 per cent of linseed oil increased the sticking of Bordeaux 8-8-50; the Iowa Experiment Station (45), that small amounts seemed effective with Bordeaux; and Hood (44), that 1 pint of linseed or fish oil in 50 gallons increased substantially the adherence of lead arsenate. Degrully (20) advocated silicic sol as a sticker for copper sprays.

The work of Guba of this Station with basic copper sulfate was conducted largely in the greenhouse on cucumbers and tomatoes with artificial rain, but also in the field with cucumbers and celery. In many instances the copper on a given area of leaf surface was determined in the laboratory by electrical deposition and calculated to 100 square inches, although substantially all of the deposit was on the upper surface. In some cases there was considerable variation in the amount of copper in duplicate applications due to unequal distribution, the impossibility of uniform washing, the small number of leaves available for analysis from greenhouse tests, loss in ashing, etc.; nevertheless the results shown in Table 2 are helpful.

Table 2.—Effect of Adhesives on Spray Residue.

Fungicide and Adhesive	Copper on Leaf Surface per 100 Square Inches		Adherence Observed after Washing (Guba)
	Deposited	After Washing	
	Grams	*Grams*	
Bordeaux mixture 4-4-50	0.0094	0.0068*	excellent
Basic copper sulfate (same concentration as Bordeaux):			
without adhesive	0.0091	0.0045*	poor to fair
with—sugar 0.10%	0.0098	0.0030	poor
wheat flour (patent) 0.10%	0.0113	0.0056	good
Tekoe flour 0.10%	....	0.0042	fair to good
Tekoe flour 0.21%	....	0.0046	fair to good
gum arabic 0.10%	0.0028*	0.0040	poor to fair
saponin 0.10%	....	0.0010	poor
glue 0.10%	0.0077	0.0037	fair to good
Laucksite 0.10%	0.0105	0.0056	....
skim milk powder 0.10%	....	0.0013	poor
semi-solid buttermilk 0.10%	....	0.0026	fair to good
calcium caseinate 0.10%	0.0071	0.0028	....
Castile soap 0.10%	0.0092	0.0050	....
rosin fish-oil soap 0.10%	0.0067	0.0032	fair
Wilkinite 0.10%	0.0099	0.0029	....
Average	0.0091	0.0035	....

*Excluded from average.

Bordeaux 4-4-50 was employed as a standard, and basic copper sulfate without adhesive as a check. The amount of copper in the unwashed spray residue was fairly constant and averaged 0.0091 grams to 100 square inches. Basic copper sulfate with and without adhesive deposited substantially as much copper as Bordeaux. The results after washing are less dependable, however, as washing was a factor impossible to control under the conditions of the experiment. Bordeaux is fairly conspicuous on the leaf surface due to the excess lime (whitewash). Guba reported the retention as "excellent", which was confirmed by the copper content. Basic copper sulfate is less visible. The adherence was reported as "poor to fair", although the copper was two-thirds that of Bordeaux. Admixtures with flour, Wilkinite and other substances increased the visibility of the residue. Sugar with basic copper sulfate was "poor" and actually reduced adherence, probably due to the formation of copper saccharate which is removed by washing and carried more or less of the insoluble portion of the fungicide. Guba employed 0.05 per cent of dextrin with basic sulfate on cucumbers and celery in the field but did not observe any increase in either spreading or adhesiveness. Flour proved a "good" adhesive, and Tekoe "fair to good" at both concentrations. The efficiency of both products might have been increased by the addition of a small amount of alkali to disperse the albuminous compounds. Gum arabic was "poor to fair" and saponin "poor."

Glue was reported "fair to good", but was more promising in field tests than the figures indicate. Laucksite, a soy-bean-fish-oil adhesive, was effective but disliked and is not obtainable in eastern markets. Skim milk powder was "poor"; semi-solid buttermilk, reported "fair to good", was ineffective; and calcium caseinate of similar character. Better dispersion might have proved of advantage. Castile soap increased adherence. Ivory soap was "fair to good"; and rosin fish-oil soap, reported "fair", was of little value as an adhesive, although 0.75 per cent (1 ounce per gallon) in field tests proved superior to 0.10 per cent glue. Wilkinite increased visibility but not adhesiveness.

Linseed oil, at the rate of 0.10 per cent, with basic copper sulfate has been employed in field experiments with various crops for two seasons. The oil disperses readily in the spray and seems to have value as a sticker. Its use on fruits has been endorsed by some members of the staff.

In Guba's experiments the addition of a small amount of properly dispersed flour, glue and Castile soap to basic copper sulfate, evidently increased the adherence, but whether this was due to better distribution, to the formation of more resistant deposits, or both, is difficult to say and likely to vary with the supplement employed and the character of the leaf surface. Reaction products such as copper albuminate, caseinate, oleate, palmitate, resinate, stearate and tannate are relatively insoluble in water and are generally considered of low fungicidal value, but in small amounts may increase the retention of the deposit on the leaves. Fineness, stability and water-resisting properties are factors to be noted. Various proprietary Bordeaux mixtures and copper hydroxide might profit by similar treatment. The time and labor required for the proper dispersion of the adhesive, however, is a feature that renders the process objectionable to most operators.

5. To prevent or reduce crystallization or decomposition by the addition of protectors.

Bordeaux mixture on standing loses its gelatinous character, settles, gradually acquires a purplish color, and the final, dense aggregates are said to be sphaero crystals of undetermined composition. Burgundy mixture undergoes a somewhat similar change and is converted into malachite. The incorporation of properly prepared protective substances may serve to prevent or, at least, retard crystallization and to preserve the highly dispersed character of the precipitate with its high power of suspension, excellent wetting and spreading properties and adhesiveness. The use of protectors with coarser suspensions probably act in a like manner but to a lower degree. Kelhofer (49) advised the addition of sugar to Bordeaux mixture to prevent crystallization, Butler (7, 8, 9) found 0.03 per cent of sugar effective, and Lutman (61) reported both sucrose and glucose efficient. The practice has become fairly well recognized for Bordeaux mixtures that have to be kept for several hours. Data on the subject are rather meager, as most copper fungicides are applied immediately after preparation.

6. To prevent or reduce interactions between fungicides and insecticides in combined sprays.

Generalizations on interactions involving so diversified products as are employed in disease and insect control are of questionable value. Most of the copper fungicides and of the stomach poison arsenicals in current use are relatively insoluble and fairly stable, but more or less subject to hydrolysis and readily decomposed by soluble compounds such as nicotine sulfate, soluble sulfides, soaps, etc. As a rule the arsenicals require more consideration than Bordeaux, Burgundy and other copper fungicides, as soluble compounds of arsenous and arsenic acids are extremely toxic to foliage. Lime-sulfur should never be combined with copper fungicides; but in the case of arsenicals, milk of lime, calcium caseinate and protective colloids in general may serve to retard objectionable reactions. The order of mixing has been emphasized by Robinson (81) and others. Some writers treat the subject as merely a matter of compatibles and noncompatibles.

7. To increase visibility of the deposit.

Bordeaux mixtures containing an excess of lime (whitewash) probably yield the most conspicuous deposits on the leaf surface covered of any of the copper fungicides. Several of the supplementary products serve to increase substantially the visibility of basic sulfate and similar fungicides, of which Wilkinite and wheat flour proved excellent.

Summary.

1. The efficiency of insoluble copper fungicides is dependent largely on the degree of dispersion and other physical characteristics, as determined by suspension, which is undoubtedly the simplest and most practical method of evaluation. Wetting, spreading and adhesiveness are so closely correlated and interdependent that complete differentiation is impossible.

2. So-called "soluble copper" is not a criterion of fungicidal activity, as various organic compounds produce filtrable copper, the activity of which is lower than that of soluble inorganic compounds which are readily ionized.

3. Suspension, although largely dependent on dispersion, may be increased in a measure by supplementary products. This is likewise true of wetting, spreading and adhesiveness.

4. Protectors may retard the formation of larger aggregates, crystallization, decomposition and the interactions between non-compatibles.

5. Of the various supplements tested by the Massachusetts Experiment Station, wheat flour, glue (or gelatine), soap and tannic acid are promising in that they seem to increase the efficiency of the spray in more than one aspect.

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Publication of this document approved by the
Commission on Administration and Finance

2 M-6-'29. No. 5972.